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(54) Detergent composition containing performance additive and copolymeric compatibilizing agent therefor.

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Description

This invention relates to the detergent utilization of certain copolymeric ingredients in a compatibilizing functionality in conjunction with performance additives. The copolymeric ingredient is prepared from an ethylenically unsaturated carboxylic acid and an ethylenically unsaturated dicarboxylic acid. Preferred monomers are acrylic and methacrylic acids on one hand and maleic and citraconic acids on the other hand. The copolymeric agent was found to be especially suitable for enhancing the compatibility of detergent additives which are known to be sensitive to various conditions inclusive of prolonged storage, temperature, alkalinity, and/or laundry conditions. In more detail, the copolymeric compatibilizing agent is capable of procuring, in contradistinction to their art-established functionality, unexpected transfer properties in relation to specific detergent additives. These transfer properties go against the prevailing opinion according to which comparable copolymeric adjuvants serve as deposition inhibitors, and consequently diminish the physical contact between detergent ingredients and e.g. the fiber.

The use of low levels of (co)polymeric additives for detergent application has been known for a long time and has found application in commercial detergent products. European Patent Application 0009171, BASF AG, published April 2, 1980 relates to the incorporation of polymaleic acid as a builder ingredient and/or as an incrustation inhibitor in detergents. European Patent Application 0025551, BASF AG, published March 25, 1981 discloses the utilization of (meth)acrylic acid—maleic acid copolymeric ingredients as incrustation inhibitors in detergent compositions. The copolymer comprises a large majority of the (meth)acrylic acid monomer FR—A—2388045, The Procter & Gamble Company, published November 17, 1978, pertains to detergent compositions containing surface-active agents, builders and a binary system based on not more than 4% of a polyphosphonate and not more than 4% of a polymeric ingredient which can be represented by the copolymers obtained from the polymerization of (meth)-acrylic acid and maleic anhydride.

German Patent Application DOS 19 59 272, Procter & Gamble European Technical Center, published July 23, 1970, relates to solid oxygen-bleach detergent compositions containing a copolymeric ingredient based on vinyl methylether and maleic anhydride. The copolymeric ingredient is claimed to provide effective active oxygen regulation.

It has now been discovered that the particular copolymeric ingredient of the invention herein can be used beneficially with a view to secure very desirable performance benefits upon use in combination with particular detergent additives with the proviso that the copolymeric ingredient is preferably used in excess levels in relation to a given performance additive.

It is an object of this invention to formulate detergent compositions having desirable performance characteristics containing specific detergent additives.

It is a further object of this invention to formulate laundry products capable of providing superior overall performance in presence of specific additives.

Brief description of the invention

It has now been discovered that markedly improved detergent compositions can be formulated containing a conventional detergent matrix in combination with detergent performance additives and a copolymeric ingredient. The performance additives are present in an amount from 0.002% to 5% by weight. The copolymeric ingredient is prepared from an ethylenically unsaturated carboxylic acid monomer having not more than five carbon atoms and from an ethylenically unsaturated dicarboxylic acid monomer having not more than six carbon atoms, whereby these monomers are copolymerized in a molar proportion of 1:4 to 4:1. The weight ratio of the copolymeric ingredient to the performance additives is from 500:1 to 1:5. Performance additives for use in combination with the copolymeric ingredients are selected from water-soluble porphine photoactivators such as mixtures of sulfonated metal phthalocyanines; and renewable polyamine or amine oxide soil release agents.

Detailed description of the invention

The invention herein comprises at least three major parameters, namely: a conventional detergent matrix comprising surface-active agents and builders; a detergent performance additive; and a specific copolymeric ingredient. The major parameters of the invention are described in more detail hereinafter.

Unless indicated to the contrary, the "percent" indications represent "percent by weight" indications. Qualitatively and quantitatively suitable surface-active agents for use herein are disclosed in U.S. Patent 4,192,761, column 3, line 49 to column 5, line 42. Qualitatively and quantitatively suitable detergent builder materials can also be taken from U.S. Patent 4,192,761, column 8, line 58 to column 9, line 68.

It goes without saying that the detergent matrix of the compositions of this invention can also contain other major components according to the particular needs and/or the physical state of the invention. In this respect, the compositions herein can be solid, pasty or liquid. Major amounts of pH regulants, inert fillers like sodium sulfate, water and/or organic solvents like hydrocarbons and/or lower alcohols can be applied as is well-known in the art. The detergent matrix can also contain major levels of bleaching agents, for example, oxygen bleach agents such as perborate, percarbonate, perpyrophosphate, persulfate, more in general, all oxygen-bleach agents which are known to be suitable for use in detergent compositions in the established levels.

The copolymeric ingredient consists of an ethylenically unsaturated monocarboxylic acid monomer having not more than 5, preferably 3 or 4, carbon atoms, and an ethylenically unsaturated dicarboxylic acid monomer having not more than 6, preferably 4 carbon atoms, whereby the molar ratio of the monomers is in the range from 1:4 to 4:1 (i.e., monocarboxylic acid:dicarboxylic acid). Suitable examples of the monocarboxylic acid monomer are: acrylic acid, methacrylic acid and vinyl acetic acid. Acrylic and methacrylic acids are preferred. Suitable examples of the dicarboxylic acid monomers are: maleic acid; fumaric acid; citraconic acid; and mesaconic acid. Preferred dicarboxylic acids are maleic acid and citraconic acid.

The copolymeric ingredient can be further defined with the aid of the calcium sequestration value. These values can be measured by nephelometric titration methods (as described in literature

—S. Chaberek and A. E. Martell, Organic Sequestering Agents, Wiley, New York, 1959;

—R. L. Smith, The Sequestration of Metals, Chapman and Hall, London, 1959):

a calcium nitrate solution is added to a solution containing sequestrant and sodium oxalate until turbidity is produced; the titration is being carried out at constant pH=10 and room temperature.

The sequestration value is expressed in mgCaCO₃/gram of copolymeric ingredient.

The calcium sequestration value of the copolymeric ingredient is preferably in the range from 300—900 mgCaCO₃/g.

The performance additives herein are present in an amount from 0.002% to 5%. Depending upon the particular functionality of the additive and the planned use of the final detergent composition, the preferred usage ranges for the individual additives vary from additive to additive. The term performance additive as used herein is meant to express that the specific ingredient is added either to cure a deficiency of the general detergent matrix and/or to provide special laundry and cleaning benefits.

A class of performance additives that can be utilized beneficially in combination with the copolymeric agent is represented by a photoactivator, also frequently termed a photosensitizer. The photoactivator is a porphine of a mono-, di-, tri-, or tetraaza porphine solubilized with anionic, nonionic, and/or cationic substituent groups and metal free or metallated with Zn(II), Ca(II), Cd(II), Mg(II), Sc(III), Al(III), or Sn(IV). Preferred metal-ions for the photoactivator are zinc and aluminum. The photoactivator is frequently used in low levels, e.g., in the level from about 20 ppm to 2000 ppm. In solid detergent compositions, the photoactivator is generally used in combination with a carrier material such as polyphosphates, sulfates, a.s.o. Generally, the level of such photoactivator particles (containing a carrier material) represents from 0.1% to 1% of the detergent composition. The photoactivator is believed to exhibit its activity in the direct environment of the fiber possibly in combination with perborate. The copolymeric ingredient favors this transfer of photoactivator to the fiber in presence of the other components in the laundry liquor at the applicable temperatures, e.g., laundry temperatures in the range from up to about 60°C or up to the boil.

As an example, a water-soluble photoactivator used in the specified levels can be represented by the porphine activators of European Patent Application 0003149. The weight ratio of copolymer to photoactivator performance additive is frequently in the range from 500:1 to 7:1.

The copolymeric ingredient was also found to be effective in combination with additive levels of renewable soil release agents as described in EP—A—0042187 and EP—A—0042188. The copolymeric ingredient enhances and contributes to a more quantitative deposition of the renewable soil release agent, specifically the polyamines oxidized or not and/or the oxidized monoamines.

The renewable soil release agent which frequently is used in levels from 0.1% to 1.5% is represented by polyamines having the formula:



wherein R is an alkyl or alkenyl group having 10 to 22 carbon atoms, the R₁'s, which are identical or different, are ethylene oxide or propylene oxide, R₂ is hydrogen, C₁₋₄ alkyl or (R₁)_y, where x, y, and z are numbers such that the sum (x+y+z) is in the range from 2 to 25, n is a number from 1 to 6 and m is a number from 1 to 9; or

amine oxides having the formula:



wherein R is an alkyl or alkenyl group having 10 to 22 carbon atoms, the R₃'s which are identical or different are selected from C₁₋₄ alkyl, ethylene oxide and propylene oxide, k is an integer from 1 to 6, l is an

integer from 0 to 6, p is 0 or 1, u, v, and w are each 1 for alkyl substituents, and integers in the range from 1 to 10 for ethylene oxide or propylene oxide substituents such that the sum of (u+v+w) is not greater than 25, with the proviso that a 1% aqueous solution of the detergent composition has an alkaline pH (20°C).

A preferred polyamine for use herein is N-hydrogenated tallow C₁₈-C₁₈-N,N',N'-tri-(2-hydroxyethyl)-propylene-1,3-diamine. Preferred amine oxide species are N-C₁₂₋₁₄-coconutalkyl-N,N-dimethyl-N-amine oxide; N-tallow C₁₈₋₁₈-alkyl-N,N',N'-tri-(2-hydroxyethyl)-propylene-1,3-diamine-N,N'-dioxide; N-C₁₂₋₁₄-alkyl-N,N',N'-tri-(2-hydroxyethyl)-propylene-1,3-diamine-N,N'-dioxide; N-C₁₈₋₁₈-tallow-alkyl-N,N-dimethyl-N-amine oxide; N-C₁₂₋₁₄-coconutalkyl-N,N-di(2-hydroxyethyl)-N-amine oxide; or N-C₁₈₋₁₈-tallowalkyl-N,N-di-(2-hydroxyethyl)-N-amine oxide. The weight ratio of copolymer to soil release additive is preferably in the range from 10:1 to 1:1.

In addition to the essential components described herereinbefore, the compositions of this invention can comprise a series of supplementary components to perfect and complement the performance advantages derived from the compositions. These additional components include brighteners, dyes, perfumes, bactericides, and antioxidants, processing aids, corrosion inhibitors, enzymes and so on. These further ingredients are used for their known functionality in the art established levels, i.e., frequently in the range from 0.1% to 5%.

The following examples illustrate the invention and facilitate its understanding.

The abbreviations for the individual ingredients have the following meaning:

- 20 LAS: Sodium salt of linear dodecyl benzene sulfonate
- TAS: Sodium salt of tallow alcohol sulfate
- FAE₃S: Sodium salt of fatty alcohol (C₁₂₋₁₈) (ethoxy)3 sulfate
- AO: C₁₂₋₁₄ alkyl dimethylamine oxide
- HLAS: Linear dodecyl benzene sulfonic acid
- 25 TAE₁₁: Tallow alcohol ethoxylated with about 11 moles of ethylene oxide
- FA₂₅E₇: Fatty alcohol (C_{12-C18}) ethoxylated with about 7 moles of ethylene oxide
- FA₂₅E₄: Fatty alcohol (C_{12-C18}) ethoxylated with about 4 moles of ethylene oxide
- CFA: C₁₂₋₁₄ coconut fatty acid
- HFA: Hydrogenerated C₁₈₋₂₂ fatty acid
- 30 STPP: Sodium tripolyphosphate
- Zeolite A: Sodium salt of zeolite 4A (average particle size between 2-6 μm)
- NTA: Sodium salt of nitrilotriacetate
- Copolymer: AA⁴⁰/MA⁶⁰=copolymer of acrylic acid 40 mol-% and maleic acid 60 mol-%
- MAA⁵⁰/MA⁵⁰=copolymer of methacrylic acid 50 mol-% and maleic acid 50 mol-%
- 35 CMC: Sodium salt of carboxymethyl cellulose
- MHPC: Sodium salt of methyl hydroxypropyl cellulose
- Silicate 1.6: Sodium silicate SiO₂/Na₂O=1.6
- TEA: triethanolamine
- STS: Sodium salt of toluene sulfonate
- 40 EDTA: Sodium salt of ethylene diamine tetra-acetate
- Perborate: NaBO₂ · H₂O₂ · 3H₂O
- P.A.: Photoactivator sulfonated Zn phthalocyanine
- SRS III: oil in water emulsion
 - 9% polydimethylsiloxane
 - 1% amorphous hydrophobic silica
 - 5% coconut fatty acid ethoxylated with 7 moles of ethylene oxide
 - 85% water
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The following granular detergent compositions are prepared by conventional spray-drying of a slurry of individual ingredients and subsequent dry-mixing of this base powder with spray-drying sensitive ingredients.

Solid detergent compositions are prepared having the following formulae.

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	Ingredients	Composition (% by weight)		
		I	II	III
5	LAS	10.0	5.0	7.0
	TAS	—	3.0	—
	FAE ₃ S	3.0	—	—
10	TAE ₁₁	1.0	1.0	2.7
	HFA	—	4.0	3.5
15	STPP	—	60.0	28.0
	NTA	—	—	4.0
	Na ₂ CO ₃	20.0	—	—
20	Copolymer MAA ⁴⁰ /MA ⁸⁰	1.7	1.4	0.3
	CMC	1.0	1.0	0.8
25	MHPC	—	0.5	—
	Silicate 1.6	18.0	3.0	8.0
	MgSO ₄	1.0	—	0.5
30	Na ₂ SO ₄	5.2	9.5	4.2
	NaOH	1.1	0.9	0.2
35	STS	1.4	—	—
	EDTA	0.2	0.3	0.3
	Perborate	25.0	—	30.0
40	P.A.	0.007	0.003	0.002
	Enzyme (proteolytic)	0.3	0.6	0.2
45	Brightener, perfume, H ₂ O		Balance to 100	

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	Ingredi nt	Composition (% by weight)			
		IV	V	VI	VII
5	LAS	7.0	4.5	7.0	4.5
	TAS	—	2.5	—	2.5
	A.O.	0.5	0.3	0.8	1.0
10	TAE ₁₁	2.7	—	2.7	—
	FA ₂₅ E ₇	—	2.0	—	2.0
15	CFA	—	2.0	—	2.0
	HFA	3.5	4.0	3.5	4.0
	STPP	31.0	24.0	16.0	8.0
20	Zeolite A	—	—	16.0	16.0
	NTA	—	4.0	—	6.0
25	Copolymer AA ⁴⁰ /MA ⁸⁰	—	1.5	—	1.5
	MAA ⁶⁵ /MA ⁴⁵	—	—	1.3	—
	AA ⁸⁰ /MA ⁸⁰	2.0	—	—	—
30	CMC	0.8	0.8	1.0	1.0
	Silicate 1.6	5.0	5.0	2.0	2.0
35	MgSO ₄	—	0.5	0.5	1.0
	Na ₂ SO ₄	7.4	10.5	8.5	11.6
	NaOH	1.3	1.0	0.8	1.0
40	EDTA	0.2	0.3	0.3	0.2
	Perborate	32.0	28.0	30.0	28.0
45	Enzyme (proteolytic)	0.2	0.2	0.3	0.2
	Brightener, perfume, water		balance to 100		
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A liquid detergent composition is made by mixing the following individual ingredients.

5	Ingredient	Composition (% by weight) VIII
	HLAS	13.5
	TAE ₁₁	20.0
10	FA ₂₅ E ₄	10.0
	Copolymer MAA ⁵⁰ /MA ⁵⁰	0.5
15	TEA	7.7
	P.A.	0.002
	Enzyme (proteolytic)	0.8
20	SRS III	1.0
	1—2 propylene glycol	2.0
25	Ethanol	11.0
	Brightener, perfume, dye, H ₂ O	balance to 100

30 Claims

1. A detergent composition with a conventional matrix on basis of surface-active agents, builders, performance additives and a copolymeric ingredient, characterized in, that the performance additive is present in an amount from 0.002% to 5% by weight, and is selected from:

35 (a) a water-soluble photoactivator from the group of porphine or mono-, di-, tri-, or tetraaza porphine solubilized with anionic, nonionic, and/or cationic substituent groups and metal free or metallated with Zn(II), Ca(II), Cd(II), Mg(II), Sc(III), Al(III) or Sn(IV); and

(b) a soil release agent which is a polyamine having the formula



45 wherein R is an alkyl or alkenyl group having 10 to 22 carbon atoms, the R₁'s, which are identical or different, are ethylene oxide or propylene oxide, R₂ is hydrogen C₁₋₄ alkyl or (R₁)_y, where x, y, and z are numbers such that the sum (x+y+z) is in the range from 2 to 25, n is a number from 1 to 6 and m is a number from 1 to about 9; or

50 an amine oxide having the formula:



60 wherein R is an alkyl or alkenyl group having 10 to 22 carbon atoms, the R₃'s which are identical or different are selected from C₁₋₄ alkyl, ethylene oxide and propylene oxide, k is an integer from 1 to 6, l is an integer from 0 to 6, p is 0 or 1, u, v, and w are each 1 for alkyl substituents, and integers in the range from 1 to 10 for ethylene oxide or propylene oxide substituents such that the sum of (u+v+w) is not greater than 25, and that the copolymeric ingredient consists of an ethylenically unsaturated monocarboxylic acid monomer having not more than 5, preferably 3 or 4, carbon atoms, and an ethylenically unsaturated dicarboxylic acid monomer having not more than 6, preferably 4, carbon atoms, whereby the molar ratio of

the monomers is in the range from 1:4 to 4:1; and whereby the weight ratio of the copolymer to the performance additive is in the range of from 500:1 to 1:5.

2. The detergent composition in accordance with Claim 1 wherein the copolymeric ingredient is comprised of (meth)acrylic acid and maleic acid monomers.

3. The detergent composition in accordance with Claim 1 wherein the photoactivator is present in an amount from 20 ppm to 2000 ppm and wherein the weight ratio of copolymer to photoactivator is in the range from 500:1 to 7:1.

4. The detergent composition in accordance with Claim 1 wherein the soil release agent is present in an amount from 0.1% to 1.5% by weight in a weight ratio of copolymer to performance additive in the range from 10:1 to 1:1, whereby a 1% aqueous solution of the detergent composition has an alkaline pH (20°C).

Patentansprüche

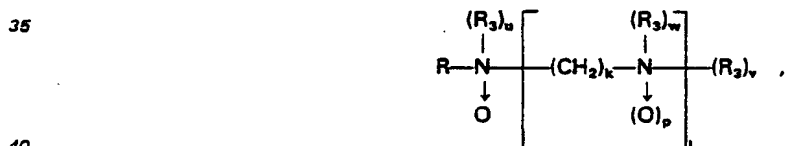
1. Eine Reinigungsmittelzusammensetzung mit einer üblichen Matrix auf Basis von grenzflächenaktiven Mitteln, Gerüststoffen, wirkungsfördernden Zusätzen und einem Copolymerbestandteil, dadurch gekennzeichnet, daß der wirkungsfördernde Zusatz in einer Menge von 0,002 Gew.-% bis 5 Gew.-% vorliegt und ausgewählt ist aus:

(a) einem wasserlöslichen Photoaktivator aus der Porphin- oder Mono-, Di-, Tri- oder Tetraazaporphingruppe, der mit anionischen, nichtionischen und/oder kationischen Substituentengruppen löslich gemacht und metallfrei oder mit Zn(II), Ca(II), Cd(II), Mg(II), Sc(III), Al(III) oder Sn(IV) metallisiert ist; und

(b) einem Schmutzfreisetzungsmittel, das ein Polyamin der Formel



worin R eine Alkyl- oder Alkenylgruppe mit 10 bis 22 Kohlenstoffatomen ist, die Reste R₁, welche gleich oder verschieden sind, Ethylenoxid oder Propylenoxid sind, R₂ Wasserstoff, C₁₋₄-Alkyl oder (R₁)_y ist, wobei x, y und z Zahlen derart sind, daß die Summe (x+y+z) im Bereich von 2 bis 25 liegt, n eine Zahl von 1 bis 6 ist, und m eine Zahl von 1 bis etwa 9 ist; oder eine Aminoxid der Formel:



worin R eine Alkyl- oder Alkenylgruppe mit 10 bis 22 Kohlenstoffatomen ist, die Reste R₃, die gleich oder verschieden sind, aus C₁₋₄-Alkyl, Ethylenoxid und Propylenoxid ausgewählt sind, k eine ganze Zahl von 1 bis 6 ist, l eine ganze Zahl von 0 bis 6 ist, p 0 oder 1 ist, und u, v und w für Alkylsubstituenten jeweils 1 sind, und derartige ganze Zahlen im Bereich von 1 bis 10 für Ethylenoxid- oder Propylenoxidsubstituenten darstellen, daß die Summe von (u+v+w) nicht mehr als 25 beträgt, ist;

und daß der Copolymerbestandteil aus einem ethylenisch ungesättigten Monocarbonsäuremonomer mit nicht mehr als 5, vorzugsweise 3 oder 4, Kohlenstoffatomen, und einem ethylenisch ungesättigten Dicarbonsäuremonomer mit nicht mehr als 6, vorzugsweise 4, Kohlenstoffatomen besteht, wobei das Molverhältnis der Monomeren im Bereich von 1:4 bis 4:1 liegt; und wobei das Gewichtsverhältnis des Copolymer zum wirkungsfördernden Zusatz im Bereich von 500:1 bis 1:5 liegt.

2. Die Reinigungsmittelzusammensetzung nach Anspruch 1, wobei der Copolymerbestandteil aus (Meth)acrylsäure- und Maleinsäuremonomeren besteht.

3. Die Reinigungsmittelzusammensetzung nach Anspruch 1, wobei der Photoaktivator in einer Menge von 20 Tpm bis 2000 Tpm vorliegt, und wobei das Gewichtsverhältnis von Copolymer zu Photoaktivator im Bereich von 500:1 bis 7:1 liegt.

4. Die Reinigungsmittelzusammensetzung nach Anspruch 1, wobei das Schmutzfreisetzungsmittel in einer Menge von 0,1 Gew.-% bis 1,5 Gew.-% bei einem Gewichtsverhältnis von Copolymer zu wirkungsförderndem Zusatz im Bereich von 10:1 bis 1:1 vorliegt, und wobei eine 1%ige wässrige Lösung der Reinigungsmittelzusammensetzung einen alkalischen pH-Wert (20°C) aufweist.

Revendications

1. Une composition détergente comprenant une matrice classique à base d'agents de surface, d'adjuvants de détergence, des additifs pour augmenter la performance et un constituant copolymérique,

caractérisée en ce que l'additif augmentant la performance est présent à la teneur de 0,002 % à 5% en poids et est choisi parmi

- a) un photo-activateur hydrosoluble du groupe de la porphine ou de la mono-, di-, tri- ou tétraazaporphine solubilisée par des groupes substituants anioniques, non ioniques et/ou cationiques et
- b) un agent éliminant les salissures qui est une polyamine répondant à la formule



dans laquelle R est un groupe alkyle ou alcényle ayant 10 à 22 atomes de carbone, les R_1 qui sont identiques ou différents, sont de l'oxyde d'éthylène ou de l'oxyde de propylène, R_2 est l'hydrogène, un alkyle en C_1 à C_4 ou $(R_1)_y$, où x, y et z sont des nombres tels que la somme $(x+y+z)$ est comprise dans la gamme de 2 à 25, n est un nombre de 1 à 6 et m est un nombre de 1 à environ 9; ou un oxyde d'amine répondant à la formule



dans laquelle R est un groupe alkyle ou alcényle ayant 10 à 22 atomes de carbone, les R_3 qui sont identiques ou différents sont choisis parmi un alkyle en C_1 à C_4 , l'oxyde d'éthylène et l'oxyde de propylène, k est un nombre entier de 1 à 6, l est un nombre entier de 0 à 6, p est 0 ou 1, u, v et w sont chacun 1 pour les substituants alkyle et des nombres entiers de 1 à 10 pour les substituants oxyde d'éthylène ou oxyde de propylène de manière que la somme de $(u+v+w)$ ne soit pas supérieure à 25, et que le constituant copolymérique consiste en un acide monocarboxylique monomère éthyléniquement insaturé n'ayant pas plus de 5, de préférence 3 ou 4 atomes de carbone et en un acide dicarboxylique monomère éthyléniquement insaturé n'ayant pas plus de 6, de préférence 4 atomes de C, moyennant quoi le rapport molaire des monomères se situe dans la gamme de 1:4 à 4:1 et le rapport pondéral du copolymère à l'additif augmentant la performance est compris dans la gamme de 500:1 à 1:5.

2. Composition détergente selon la revendication 1, dans laquelle le constituant copolymérique comprend de l'acide (meth)-acrylique et de l'acide maléique comme monomères.

3. Composition détergente selon la revendication 1, dans laquelle le photo-activateur est présent en quantité de 20 ppm à 2000 ppm et le rapport pondéral de copolymère à photo-activateur se situe dans la gamme de 500:1 à 7:1.

4. Composition détergente selon la revendication 1, dans laquelle l'agent éliminant les salissures est présent à la teneur de 0,1% à 1,5% en poids dans un rapport pondéral de copolymère à additif augmentant la performance s'étendant de 10:1 à 1:1, moyennant quoi une solution aqueuse à 1% de la composition détergente possède un pH alcalin (à 20°C).